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EXTREMES IN OXIDIZING POWER, ACIDITY, AND BASICITY

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**10/01/2013**
**Final Report**

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**14. ABSTRACT**

Professor Michl and collaborators prepared several icosahedral monocarba-closo-dodecaborate anions carrying halogen and trifluoromethyl substituents and investigated their oxidation by chemical and electrochemical means and by quantum chemical calculations. These anions are of interest for fuel cell and high-voltage battery applications, because they are unusually weakly nucleophilic and extremely difficult to oxidize, with reversible redox potentials calculated up to 5 V above ferrocene/ferricenium. In liquid sulfur dioxide, the standard solvent for electrochemical oxidation at highly positive potentials, all oxidations were irreversible. In 1,1,1,3,3,3-hexafluoroisopropan-2-ol, the undecafluorinated anion is oxidized reversibly at 2.43 V above ferrocene/ferricenium (calculated 2.40 V) but the radical is too unstable for isolation. Other undecahalogenated anions are oxidized irreversibly. A promising new solvent that dissolves supporting electrolytes and resists oxidation is 1,1,1,3,3-pentafluorobutane. In two cases, the oxidized neutral radicals were sufficiently stable in perfluorohexane solution for spectroscopic characterization, but only up to -40 degrees C. At temperatures closer to ambient, this solvent was oxidized.

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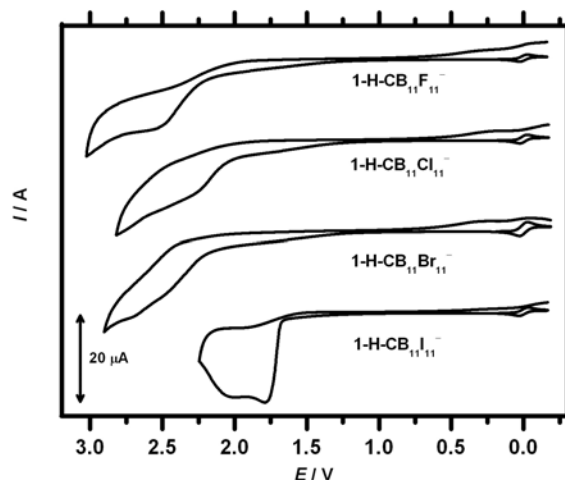| 16. SECURITY CLASSIFICATION OF: | | | 17. LIMITATION OF ABSTRACT | 18. NUMBER OF PAGES | 19a. NAME OF RESPONSIBLE PERSON |
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Summary

Professor Michl and collaborators prepared several icosahedral monocarba-*closo*-dodecaborate anions carrying halogen and trifluoromethyl substituents and investigated their oxidation by chemical and electrochemical means and by quantum chemical calculations. These anions are of interest for fuel cell and high-voltage battery applications, because they are unusually weakly nucleophilic and extremely difficult to oxidize, with reversible redox potentials calculated up to 5 V above ferrocene/ferricenium. In liquid sulfur dioxide, the standard solvent for electrochemical oxidation at highly positive potentials, all oxidations were irreversible. In 1,1,1,3,3,3-hexafluoroisopropan-2-ol, the undecafluorinated anion is oxidized reversibly at 2.43 V above ferrocene/ferricenium (calculated 2.40 V) but the radical is too unstable for isolation. Other undecahalogenated anions are oxidized irreversibly. A promising new solvent that dissolves supporting electrolytes and resists oxidation is 1,1,1,3,3-pentafluorobutane. In two cases, the oxidized neutral radicals were sufficiently stable in perfluorohexane solution for spectroscopic characterization, but only up to -40 degrees C. At temperatures closer to ambient, this solvent was oxidized. Upon oxidation of iodine-substituted anions an iodine atom is lost, ultimately yielding molecular iodine, while the carborane cage with one naked vertex adds to the starting anion to yield an iodonium salt carrying two carborane cages on an iodine atom.

Report

In the following, the salient results of our investigation are outlined.

1. A fluorine line was rebuilt and modernized. Additional safety features were introduced.

2. The syntheses of four highly trifluoromethylated anions $HCB_{11}(CF_3)_nF_{11-n}^-$ ($n = 5, 6, 10$, and 11) and preliminary observations of the electroneutral radical analogs of two of them ($n = 5, 6$) have been published [Fete, M. G.; Havlas, Z.; Michl, J. "$HCB_{11}(CF_3)_nF_{11-n}^-$: Inert Anions with High Anodic Oxidation Potentials", *J. Am. Chem. Soc.* **2011**, *133*, 4123].

3. The literature procedure for the undecafluorination of $CB_{11}H_{12}^-$ salts was improved considerably. The new procedure provides a reproducible 75 - 85% yield of $HCB_{11}F_{11}^-$ [Valášek, M.; Šembera, F.; Hughes, M. J.; Stibor, I.; Janoušek, Z.; Michl, J. "Synthesis of Cs[1-H-$CB_{11}F_{11}$]", in *Efficient Preparation of Fluorine Compounds*, Roesky, H. W., Ed. **2012** John Wiley & Sons: Hoboken, NJ, p 22].

4. The literature procedure for the iodination of $CB_{11}H_{12}^-$ salts was greatly simplified and $HCB_{11}I_{11}^-$ is now easily available on a 10 g scale. The hope that its fluorination may provide an even better route to $HCB_{11}F_{11}^-$ was not fulfilled, since explosive intermediates were formed.

5. The more easily accessible remaining members of the $HCB_{11}X_{11}^-$ series (X = Cl, Br) were also prepared and the anodic electrochemistry of all four anions was examined in liquid $SO_2$, the standard solvent for electrochemical oxidation at high redox potentials. Initial one-electron oxidation to the presumed electroneutral radicals $HCB_{11}X_{11}^\bullet$ (X = F, Cl, Br, I) was found to be irreversible (Figure 1). The redox potentials in liquid $SO_2$ at -65 °C are 2.61, 2.40, 2.56, and 1.79

V relative to ferrocene/ferricenium, respectively. The order of these values does not follow the electronegativity of halogens and thus is not intuitive.



**Figure 1**. Cyclic voltammetry of $HCB_{11}X_{11}^-$ anions in liquid $SO_2$ at $-65\ °C$ (2-3 mM, vs. $Fc/Fc^+$, 0.1 M TBA HFP).

6. The nature of the processes that are responsible for the irreversibility appears to vary somewhat for different members of the series, and this may account for $HCB_{11}Br_{11}^-$ being harder to oxidize than $HCB_{11}Cl_{11}^-$ and only slightly easier than $HCB_{11}F_{11}^-$. Our examination of other $HCB_{11}H_{11}^-$ anions that carry an iodine substituent suggests that $HCB_{11}I_{11}^-$ is oxidized to a radical that falls apart spontaneously into an iodine atom, which ultimately yields $I_2$, plus the novel and highly reactive neutral ylide $HCB_{11}I_{10}$ with a naked boron vertex, which adds to $HCB_{11}I_{11}^-$ to form an iodonium ylide. In contrast, we believe that the $HCB_{11}F_{11}^{\bullet}$ and $HCB_{11}Cl_{11}^{\bullet}$ radicals transfer a halogen to $SO_2$ and ultimately yield sulfuryl fluoride and sulfuryl chloride, respectively, again leaving behind the corresponding novel naked vertex species $HCB_{11}X_{10}$, which is unstable. The behavior of $HCB_{11}Br_{11}^{\bullet}$ is unclear. We originally hoped that a different solvent can be found in which the strongly oxidizing radicals $HCB_{11}F_{11}^{\bullet}$ and $HCB_{11}Cl_{11}^{\bullet}$, and possibly also $HCB_{11}Br_{11}^{\bullet}$, are stable and can be used as reagents. This hope has not been fulfilled and we have concluded that these readicals are insufficiently sterically hindered to prevent dimerization and other destructive processes.

7. Much of our expectation is based on the results obtained for the electrochemical oxidation of the simpler anion $12\text{-}I\text{-}HCB_{11}Me_{10}^-$ that carries a single iodine atom. The product of the secondary reactions of the naked vertex ylide $HCB_{11}Me_{10}$ formed by the loss of an iodine atom from the initially formed unstable radical $12\text{-}I\text{-}HCB_{11}Me_{10}^{\bullet}$ has been spectroscopically identified as the iodonium ylide $[(12\text{-}HCB_{11}Me_{10})_2I]^-$ that results from the trapping of $HCB_{11}Me_{10}$ with the starting anion, $12\text{-}I\text{-}HCB_{11}Me_{10}^-$. This highly sterically strained iodonium ylide is the first example of a species with a single atom (iodine) carrying two icosahedral carboranyl substituents strongly hindered by full methylation around their position of substitution (12). The DFT calculated $\sim 130°$

2

valence angle at iodine is much higher than the normally anticipated ~90° and we are presently attempting to obtain a single crystal for an X-ray analysis. The presence of strain is reflected in the reactivity of the iodonium ylide $[(12\text{-}HCB_{11}Me_{10})_2I]^-$, which releases the naked vertex species $HCB_{11}Me_{10}$ upon heating and thus promises to represent a suitable store for it. Thus, in hot aqueous solution, $[(12\text{-}HCB_{11}Me_{10})_2I]^-$ is converted into a mixture of $12\text{-}I\text{-}HCB_{11}Me_{10}^-$ with the new anion $12\text{-}HO\text{-}HCB_{11}Me_{10}^-$.

8. DFT (PCM-M06-2X/cc-pVTZ//M06-2X/cc-pVTZ) calculations of redox potentials have been performed for two dozen halogenated $CB_{11}$ anions in liquid $SO_2$, simulated by acetone for the purposes of the calculation (Table 1, values relative to ferrocene/ferricinium; cf. Figure 1). The range of the calculated potentials is impressive. Below, we express these potentials relative to $CB_{11}Me_{12}{}^\bullet$, which is 1.16 V above $Fc/Fc^+$ in liquid $SO_2$ and thus in itself a fairly strong oxidant. The radical $HCB_{11}F_5(CF_3)_6{}^\bullet$ (with a redox potential calculated at 3.0 V above $CB_{11}Me_{12}{}^\bullet$) is such an extremely strong oxidant that above -40 °C it attacks perfluorohexane. Therefore, we looked for somewhat weaker oxidants, for which it would be easier to find inert solvents. Based on the computational results, we began with an examination of $HCB_{11}Hal_{11}{}^\bullet$. When Hal = F, the redox potential is calculated to be 'only' 1.45 V above $CB_{11}Me_{12}{}^\bullet$ and surprisingly, when Hal = Cl or Br, it is even somewhat higher, 1.65 V above $CB_{11}Me_{12}{}^\bullet$. This is presumably due to less efficient $\pi$-donation from the lone pairs of these halogens. It is difficult to compare these results quantitatively with the oxidation potentials reported above, since the latter are irreversible.

**Table 1. Calculated redox potentials**

| Molecule | $-\varepsilon_{HOMO}{}^a$ | $E_{1/2}{}^a$ | $-\varepsilon_{HOMO}{}^b$ | $E_{1/2}{}^b$ | $\Delta E^a$ | $E_{1/2}{}^a$ | $\Delta E^b$ | $E_{1/2}{}^b$ | TEC | $E_{1/2}{}^a$ | $E_{1/2}{}^b$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $1,12\text{-}(NMe_2)_2\text{-}CB_{11}Me_{10}$ (1) | 5.733 | -0.32 | 5.774 | -0.29 | 4.338 | -0.71 | 4.370 | -0.68 | -0.015 | -0.61 | -0.59 |
| $1,12\text{-}(NH_2)_2\text{-}CB_{11}Me_{10}$ (2) | 6.616 | 0.57 | 6.715 | 0.65 | 5.182 | 0.14 | 5.251 | 0.20 | -0.038 | 0.21 | 0.27 |
| $1,12\text{-}(MeO)_2\text{-}CB_{11}Me_{10}$ (3) | 6.860 | 0.81 | 6.910 | 0.84 | 5.747 | 0.70 | 5.783 | 0.73 | -0.072 | 0.74 | 0.77 |
| $1,12\text{-}F_2\text{-}CB_{11}Me_{10}$ (4) | 7.527 | 1.48 | 7.562 | 1.50 | 6.483 | 1.44 | 6.524 | 1.47 | -0.147 | 1.40 | 1.43 |
| $CB_{11}Me_{12}$ (5) | 7.211 | 1.16 | 7.225 | 1.16 | 6.205 | 1.16 | 6.214 | 1.16 | -0.108 | 1.16 | 1.16 |
| $CB_{11}H_{12}$ (6) | 8.633 | 2.58 | 8.636 | 2.57 | 7.318 | 2.27 | 7.318 | 2.26 | -0.218 | 2.16 | 2.16 |
| $CB_{11}F_{12}$ (7) | 8.815 | 2.76 | 9.084 | 3.02 | 7.801 | 2.76 | 8.007 | 2.95 | -0.171 | 2.69 | 2.89 |
| $CB_{11}Cl_{12}$ (8) | 9.015 | 2.96 | 8.978 | 2.91 | 8.061 | 3.02 | 8.024 | 2.97 | -0.146 | 2.98 | 2.93 |
| $CB_{11}Br_{12}$ (9) | 8.765 | 2.71 | 8.780 | 2.73 | 7.912 | 2.87 | 7.939 | 2.88 | -0.159 | 2.82 | 2.83 |
| $CB_{11}I_{12}$ (10) | 7.844 | 1.79 | ----- | ----- | 6.955 | 1.91 | ----- | ----- | -0.033 | 1.99 | ----- |
| $1\text{-}H\text{-}(2\text{-}6)\text{-}F_5\text{-}CB_{11}(CF_3)_6$ (11) | 10.020 | 3.97 | 10.275 | 4.21 | 8.992 | 3.95 | 9.196 | 4.14 | -0.130 | 3.92 | 4.12 |
| $CB_{11}(CF_3)_{12}$ (12) | 11.451 | 5.40 | 11.723 | 5.66 | 9.990 | 4.94 | 10.178 | 5.12 | -0.106 | 4.95 | 5.13 |
| $CB_{11}(BF_2)_{12}$ (13) | 9.613 | 3.56 | 9.772 | 3.71 | 8.378 | 3.32 | 8.532 | 3.48 | -0.026 | 3.41 | 3.56 |

[a] 6-311G** basis set; [b] 6-311++G** basis set; $\varepsilon_{HOMO}$ is the anion HOMO energy; $\Delta E$ is the adiabatic detachment energy of the anion in solvent (acetone, $\varepsilon = 23.7$); $E_{1/2}$ is the oxidation potential relative to the value observed for $CB_{11}Me_{12}{}^-$; TEC denotes 6-311G** thermal and entropic contributions at -65 °C.
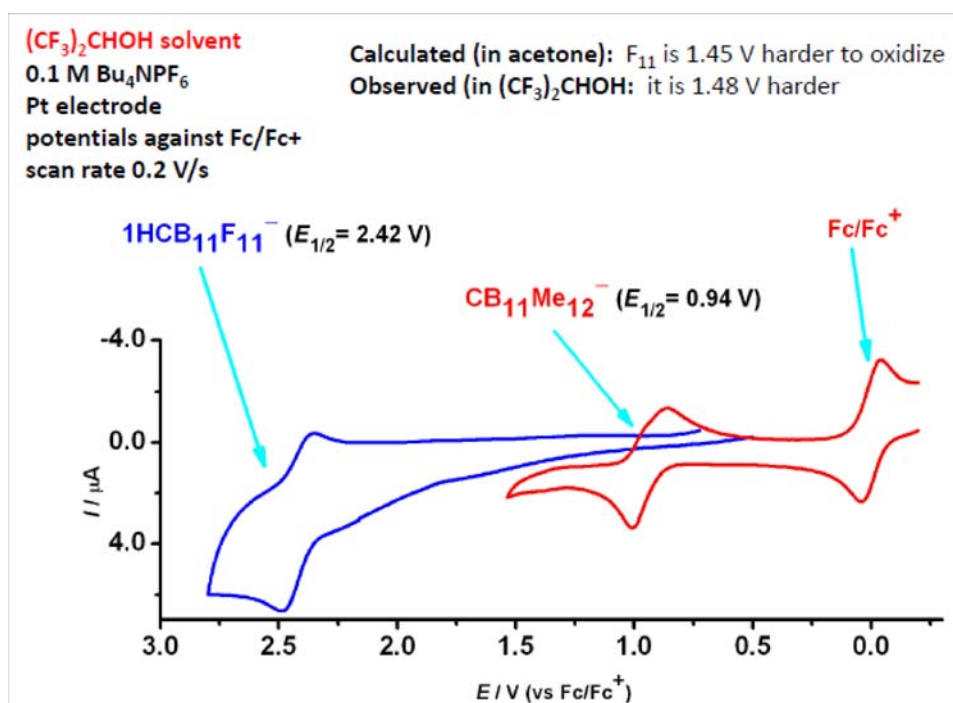
9. The lower electronegativity of Hal = I is reflected in the calculated redox potential of only 0.65 V above $CB_{11}Me_{12}{}^\bullet$. This radical has an electronic structure reminiscent of an antihydrogen atom: a negative charge delocalized on a central $CB_{11}$ core is surrounded by a spherical sheet of positive charge delocalized over the overlapping iodine lone pairs. The delocalization is of the dynamic Jahn-Teller type, with shallow minima in the potential energy surface corresponding to partial charge localization.

10. Since liquid $SO_2$ turned out to be unsuitable for our purposes, we started a search for a more inert solvent. We found that in $(CF_3)_2CHOH$, the oxidation of $HCB_{11}Hal_{11}^-$ is reversible and diffusion controlled at 1.48 V above $CB_{11}Me_{12}{}^\bullet$ when Hal = F, and this value compares well with the calculated difference of 1.45 V, strengthening our confidence in the reliability of the extraordinarily

high redox potential values calculated for anions carrying $CF_3$ groups (Table 1, Figure 1). The cyclic voltammogram is shown in Figure 2; the peak height is proportional to substrate concentration and to the square root of scan velocity, as expected for a diffusion controlled process. In this solvent, the redox potential of $CB_{11}Me_{12}^{\bullet}$ is 0.95 V above $Fc/Fc^+$. When Hal = Cl, Br, or I, the oxidation is not reversible (Figure 3). The irreversible oxidation potentials are 1.49, 1.54, or 0.87 V relative to $CB_{11}Me_{12}^{\bullet}$, respectively.

11. The result for Hal = F suggested that the radical $HCB_{11}F_{11}^{\bullet}$ might be sufficiently stable in $(CF_3)_2CHOH$ for spectroscopy and isolation. Unfortunately, this is not the case and we were unable to accumulate it as a stable species in this solvent, either.

Simultaneously with the exploration of electrochemical routes to $CB_{11}F_{12}^{\bullet}$, we attempted chemical oxidation. However, all attempts at chemical oxidation of a salt of $HCB_{11}F_{11}^{-}$ to $HCB_{11}F_{11}^{\bullet}$ in liquid HF were unsuccessful. In some cases ($F_2$, $XeF_2$) there was no reaction, and in others ($K_2NiF_6$, $NiF_3^+$, $AgF_2$, $AgF_3$) overoxidation to $BF_4^-$ occurred. We concluded that this radical does not have sufficient stability to be isolable, perhaps because fluorine substitution does not provide sufficient steric hindrance, similarly as is the case for $HCB_{11}H_{11}^{\bullet}$.



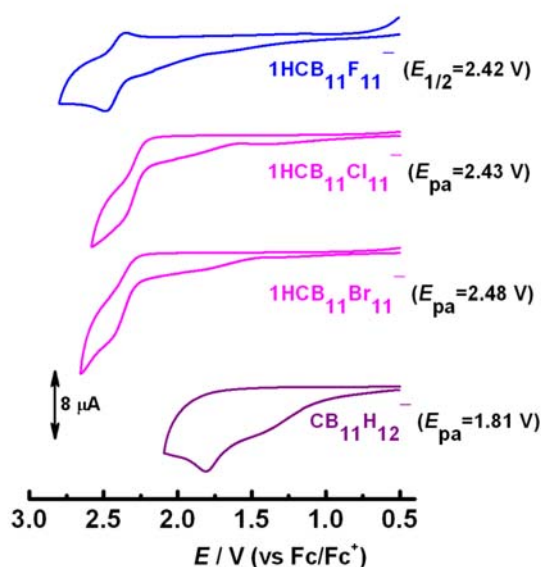**Figure 2.** Anodic oxidation of $1\text{-}H\text{-}CB_{11}F_{11}^{-}$ and $CB_{11}Me_{12}^{-}$.

12. The $(CF_3)_2CHOH$ solvent is not ideal for our purposes at any rate, since it carries both an abstractable hydrogen and an acidic hydrogen, and also a weakly nucleophilic electron lone pair on oxygen. We therefore continued our search for a truly inert solvent suitable for electrochemistry at very positive potentials. The choices are severely limited by the requirement of electrical conductivity in the presence of a suitable inert salt, which is necessary for preparative electrochemistry. Most recently, we discovered a new solvent suitable for electrochemical oxidation of our anions that dissolves a supporting electrolyte and promises to be much more inert. This is

1,1,1,3,3-pentafluorobutane, and we obtained promising initial results from our attempts to purify the commercial product from oxidizable impurities by treatment with $K_2NiF_6$.

13.    Having been thwarted in our attempts to prepare a stable radical of the undecahalogenated carborane type, we turned to anions with even more positive redox potentials, fully aware of the increased demands on the solvent.  We are presently trying to obtain an anodic cyclic voltammogram of $HCB_{11}F_5(CF_3)_6^-$ in various solvents, especially 1,1,1,3,3-pentafluorobutane. Steric hindrance by the bulky $CF_3$ groups gives us hope that the oxidation will be reversible and will produce the radical $HCB_{11}F_5(CF_3)_6^{\bullet}$ under conditions where it will be stable even at room temperature.



**Figure 3.** Cyclic voltammograms in 1,1,1,3,3-hexafluoropropan-2-ol with 0.1 M $Bu_4N\,PF_6$ (Pt electrode, scan 0.2 V/s, potentials relative to ferrocene/ferricenium).

14.  Some of the work reported here was performed in collaboration with the groups of Prof. R. Crespo at the University of Valencia, Spain, and of Dr. J. Ludvík at the Czech Academy of Sciences in Prague, Czech Republic.

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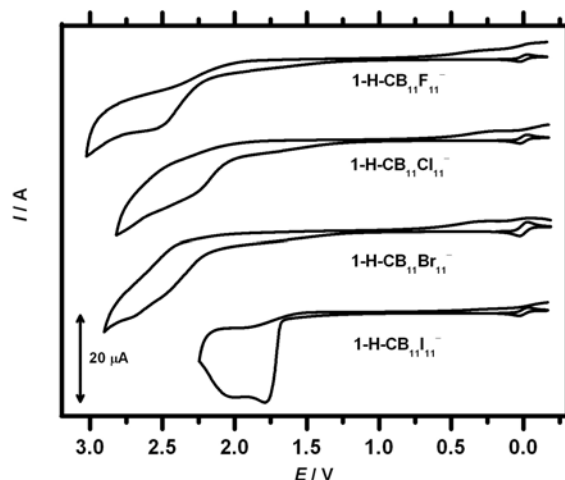7/1/10-6/30/13
Josef Michl, PI

Summary

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valence angle at iodine is much higher than the normally anticipated ~90° and we are presently attempting to obtain a single crystal for an X-ray analysis. The presence of strain is reflected in the reactivity of the iodonium ylide $[(12\text{-}HCB_{11}Me_{10})_2I]^-$, which releases the naked vertex species $HCB_{11}Me_{10}$ upon heating and thus promises to represent a suitable store for it. Thus, in hot aqueous solution, $[(12\text{-}HCB_{11}Me_{10})_2I]^-$ is converted into a mixture of $12\text{-}I\text{-}HCB_{11}Me_{10}^-$ with the new anion $12\text{-}HO\text{-}HCB_{11}Me_{10}^-$.

8. DFT (PCM-M06-2X/cc-pVTZ//M06-2X/cc-pVTZ) calculations of redox potentials have been performed for two dozen halogenated $CB_{11}$ anions in liquid $SO_2$, simulated by acetone for the purposes of the calculation (Table 1, values relative to ferrocene/ferricinium; cf. Figure 1). The range of the calculated potentials is impressive. Below, we express these potentials relative to $CB_{11}Me_{12}^{\bullet}$, which is 1.16 V above Fc/Fc$^+$ in liquid $SO_2$ and thus in itself a fairly strong oxidant. The radical $HCB_{11}F_5(CF_3)_6^{\bullet}$ (with a redox potential calculated at 3.0 V above $CB_{11}Me_{12}^{\bullet}$) is such an extremely strong oxidant that above -40 °C it attacks perfluorohexane. Therefore, we looked for somewhat weaker oxidants, for which it would be easier to find inert solvents. Based on the computational results, we began with an examination of $HCB_{11}Hal_{11}^{\bullet}$. When Hal = F, the redox potential is calculated to be 'only' 1.45 V above $CB_{11}Me_{12}^{\bullet}$ and surprisingly, when Hal = Cl or Br, it is even somewhat higher, 1.65 V above $CB_{11}Me_{12}^{\bullet}$. This is presumably due to less efficient π-donation from the lone pairs of these halogens. It is difficult to compare these results quantitatively with the oxidation potentials reported above, since the latter are irreversible.

**Table 1. Calculated redox potentials**

| Molecule | $-\varepsilon_{HOMO}$[a] | $E_{1/2}$[a] | $-\varepsilon_{HOMO}$[b] | $E_{1/2}$[b] | $\Delta E$[a] | $E_{1/2}$[a] | $\Delta E$[b] | $E_{1/2}$[b] | TEC | $E_{1/2}$[a] | $E_{1/2}$[b] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1,12-(NMe$_2$)$_2$-CB$_{11}$Me$_{10}$ (1) | 5.733 | -0.32 | 5.774 | -0.29 | 4.338 | -0.71 | 4.370 | -0.68 | -0.015 | -0.61 | -0.59 |
| 1,12-(NH$_2$)$_2$-CB$_{11}$Me$_{10}$ (2) | 6.616 | 0.57 | 6.715 | 0.65 | 5.182 | 0.14 | 5.251 | 0.20 | -0.038 | 0.21 | 0.27 |
| 1,12-(MeO)$_2$-CB$_{11}$Me$_{10}$ (3) | 6.860 | 0.81 | 6.910 | 0.84 | 5.747 | 0.70 | 5.783 | 0.73 | -0.072 | 0.74 | 0.77 |
| 1,12-F$_2$-CB$_{11}$Me$_{10}$ (4) | 7.527 | 1.48 | 7.562 | 1.50 | 6.483 | 1.44 | 6.524 | 1.47 | -0.147 | 1.40 | 1.43 |
| CB$_{11}$Me$_{12}$ (5) | 7.211 | 1.16 | 7.225 | 1.16 | 6.205 | 1.16 | 6.214 | 1.16 | -0.108 | 1.16 | 1.16 |
| CB$_{11}$H$_{12}$ (6) | 8.633 | 2.58 | 8.636 | 2.57 | 7.318 | 2.27 | 7.318 | 2.26 | -0.218 | 2.16 | 2.16 |
| CB$_{11}$F$_{12}$ (7) | 8.815 | 2.76 | 9.084 | 3.02 | 7.801 | 2.76 | 8.007 | 2.95 | -0.171 | 2.69 | 2.89 |
| CB$_{11}$Cl$_{12}$ (8) | 9.015 | 2.96 | 8.978 | 2.91 | 8.061 | 3.02 | 8.024 | 2.97 | -0.146 | 2.98 | 2.93 |
| CB$_{11}$Br$_{12}$ (9) | 8.765 | 2.71 | 8.780 | 2.73 | 7.912 | 2.87 | 7.939 | 2.88 | -0.159 | 2.82 | 2.83 |
| CB$_{11}$I$_{12}$ (10) | 7.844 | 1.79 | ----- | ----- | 6.955 | 1.91 | ----- | ----- | -0.033 | 1.99 | ----- |
| 1-H-(2-6)-F$_5$-CB$_{11}$(CF$_3$)$_6$ (11) | 10.020 | 3.97 | 10.275 | 4.21 | 8.992 | 3.95 | 9.196 | 4.14 | -0.130 | 3.92 | 4.12 |
| CB$_{11}$(CF$_3$)$_{12}$ (12) | 11.451 | 5.40 | 11.723 | 5.66 | 9.990 | 4.94 | 10.178 | 5.12 | -0.106 | 4.95 | 5.13 |
| CB$_{11}$(BF$_2$)$_{12}$ (13) | 9.613 | 3.56 | 9.772 | 3.71 | 8.378 | 3.32 | 8.532 | 3.48 | -0.026 | 3.41 | 3.56 |

[a] 6-311G** basis set; [b] 6-311++G** basis set; $\varepsilon_{HOMO}$ is the anion HOMO energy; $\Delta E$ is the adiabatic detachment energy of the anion in solvent (acetone, $\varepsilon$=23.7); $E_{1/2}$ is the oxidation potential relative to the value observed for $CB_{11}Me_{12}^{\bullet}$; TEC denotes 6-311G** thermal and entropic contributions at -65 °C.
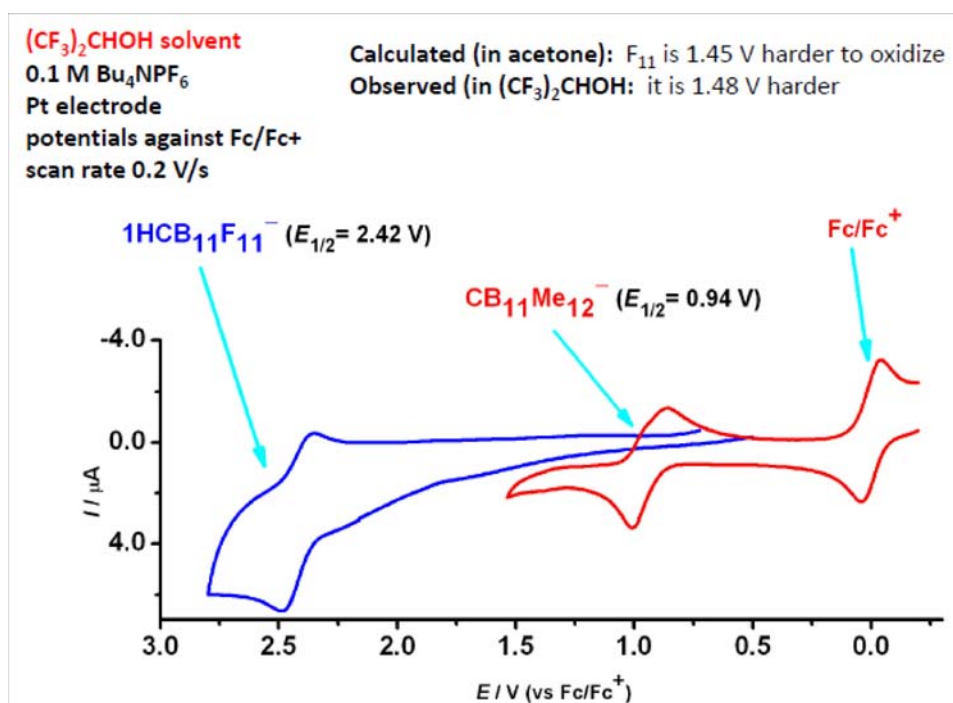
9. The lower electronegativity of Hal = I is reflected in the calculated redox potential of only 0.65 V above $CB_{11}Me_{12}^{\bullet}$. This radical has an electronic structure reminiscent of an antihydrogen atom: a negative charge delocalized on a central $CB_{11}$ core is surrounded by a spherical sheet of positive charge delocalized over the overlapping iodine lone pairs. The delocalization is of the dynamic Jahn-Teller type, with shallow minima in the potential energy surface corresponding to partial charge localization.

10. Since liquid $SO_2$ turned out to be unsuitable for our purposes, we started a search for a more inert solvent. We found that in $(CF_3)_2CHOH$, the oxidation of $HCB_{11}Hal_{11}^-$ is reversible and diffusion controlled at 1.48 V above $CB_{11}Me_{12}^{\bullet}$ when Hal = F, and this value compares well with the calculated difference of 1.45 V, strengthening our confidence in the reliability of the extraordinarily

high redox potential values calculated for anions carrying $CF_3$ groups (Table 1, Figure 1). The cyclic voltammogram is shown in Figure 2; the peak height is proportional to substrate concentration and to the square root of scan velocity, as expected for a diffusion controlled process. In this solvent, the redox potential of $CB_{11}Me_{12}{}^\bullet$ is 0.95 V above $Fc/Fc^+$. When Hal = Cl, Br, or I, the oxidation is not reversible (Figure 3). The irreversible oxidation potentials are 1.49, 1.54, or 0.87 V relative to $CB_{11}Me_{12}{}^\bullet$, respectively.

11. The result for Hal = F suggested that the radical $HCB_{11}F_{11}{}^\bullet$ might be sufficiently stable in $(CF_3)_2CHOH$ for spectroscopy and isolation. Unfortunately, this is not the case and we were unable to accumulate it as a stable species in this solvent, either.

Simultaneously with the exploration of electrochemical routes to $CB_{11}F_{12}{}^\bullet$, we attempted chemical oxidation. However, all attempts at chemical oxidation of a salt of $HCB_{11}F_{11}{}^-$ to $HCB_{11}F_{11}{}^\bullet$ in liquid HF were unsuccessful. In some cases ($F_2$, $XeF_2$) there was no reaction, and in others ($K_2NiF_6$, $NiF_3{}^+$, $AgF_2$, $AgF_3$) overoxidation to $BF_4{}^-$ occurred. We concluded that this radical does not have sufficient stability to be isolable, perhaps because fluorine substitution does not provide sufficient steric hindrance, similarly as is the case for $HCB_{11}H_{11}{}^\bullet$.
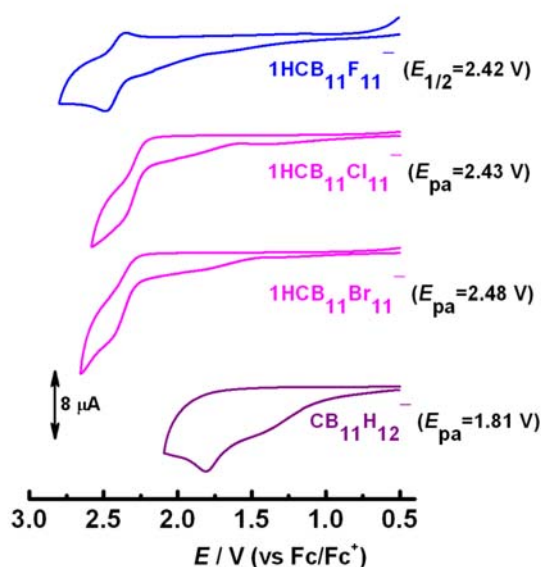


**Figure 2.** Anodic oxidation of $1\text{-}H\text{-}CB_{11}F_{11}{}^-$ and $CB_{11}Me_{12}{}^-$.

12. The $(CF_3)_2CHOH$ solvent is not ideal for our purposes at any rate, since it carries both an abstractable hydrogen and an acidic hydrogen, and also a weakly nucleophilic electron lone pair on oxygen. We therefore continued our search for a truly inert solvent suitable for electrochemistry at very positive potentials. The choices are severely limited by the requirement of electrical conductivity in the presence of a suitable inert salt, which is necessary for preparative electrochemistry. Most recently, we discovered a new solvent suitable for electrochemical oxidation of our anions that dissolves a supporting electrolyte and promises to be much more inert. This is

1,1,1,3,3-pentafluorobutane, and we obtained promising initial results from our attempts to purify the commercial product from oxidizable impurities by treatment with $K_2NiF_6$.

13. Having been thwarted in our attempts to prepare a stable radical of the undecahalogenated carborane type, we turned to anions with even more positive redox potentials, fully aware of the increased demands on the solvent. We are presently trying to obtain an anodic cyclic voltammogram of $HCB_{11}F_5(CF_3)_6^-$ in various solvents, especially 1,1,1,3,3-pentafluorobutane. Steric hindrance by the bulky $CF_3$ groups gives us hope that the oxidation will be reversible and will produce the radical $HCB_{11}F_5(CF_3)_6^\bullet$ under conditions where it will be stable even at room temperature.



**Figure 3.** Cyclic voltammograms in 1,1,1,3,3-hexafluoropropan-2-ol with 0.1 M $Bu_4N$ $PF_6$ (Pt electrode, scan 0.2 V/s, potentials relative to ferrocene/ferricenium).

14. Some of the work reported here was performed in collaboration with the groups of Prof. R. Crespo at the University of Valencia, Spain, and of Dr. J. Ludvík at the Czech Academy of Sciences in Prague, Czech Republic.